# Macrocyclic Helicates: Complexes of a 34-Membered Schiff-base Ligand

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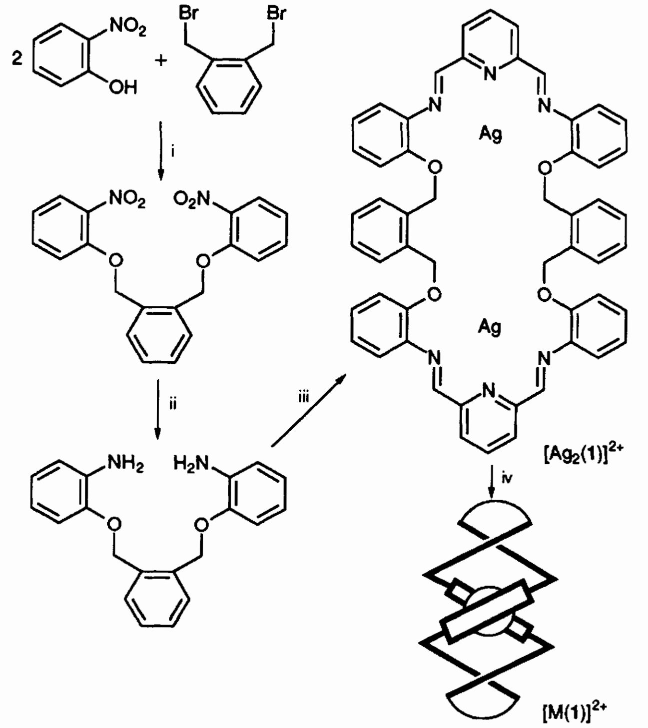
A unique double helical macrocyclic configuration of a new 34-membered Schiff-base macrocycle results from convergence of its two pyridine-2,6-diyldiimine units for meridional coordination of divalent metal ions; X-ray structure analysis establishes the cobalt(II), nickel(II) and zinc(II) complexes as the first structurally characterised macrocyclic helicates.

Interest in inorganic helical complexes—the helicates—derives from their intrinsic chirality and their potential for yielding materials with novel chemical, electronic, biological or topological properties.[1,2] We report the synthesis of a new 34-membered tetraimine macrocycle **1** which shows a predilection for adopting a double helical configuration in forming mononuclear complexes (Scheme 1). Although double- and triple-stranded helicates featuring pyridine- and 2,2′-bipyridine-based open-chain ligands have been extensively studied[3,4] and a number of other linear ligand architectures producing helical configurations in their complexes have been reported,[5] these are the first examples where a full double helical array has been structurally characterised in a macrocyclic metal complex. The only other example of a fully helical macrocyclic ligand system has been reported recently by Cram *et al.* and although no X-ray data are available, it has been deduced that its $Na^I$ and $Cu^I$ complexes feature a double helical array derived from 'crossed' phenanthroline residues.[6]

The ligand **1** sustains a full double helix in its mononuclear complexes with $Co^{II}$, $Ni^{II}$ and $Zn^{II}$ (Fig. 1) and X-ray structure analysis† confirms that meridional arrangement of pyridine-2,6-diyldiimine units, giving an approximately $D_2$ metal coordination sphere, acts as a novel six-coordinate nucleus for development of molecular helicity. The fragment of double helix initiated by incorporation of such a nucleus in a macrocyclic ligand is extended by the semi-rigid backbone of the macrocycle, giving a compressed configuration of the inner great ring which corresponds to two helical strands bridged by the methylene carbons C(5b) and C(5b′). The axis of the double helix is perpendicular to the $C_2$ axis of the complex, passes through the metal atom and lies close to the bridgehead methylene carbon atoms.

The mononuclear complexes $[Co(\mathbf{1})]^{2+}$, $[Ni(\mathbf{1})]^{2+}$ and $[Zn(\mathbf{1})]^{2+}$ are approximately isostructural in the solid state, with the metal ions in very distorted octahedral coordination geometries. The planes of the $N_3$ donors of the two essentially planar, meridional pyridinediyldiimine head units deviate from mutually orthogonal dispositions and are drawn towards each other, to a different extent in each compound (Fig. 1), so that the *trans* N(1)–M–N(1′) angle is significantly smaller than 180°. Such distortion is absent in related complexes of more flexible pyridine-2,6-diyldiimine ligand systems,[7] evidence that the stereochemical preferences of **1** compete with the geometrical requirements of the metals in determining the overall structure of the complexes; significantly the $Ni^{II}$ complex shows the least distortion to the metal coordination sphere (Fig. 1). Examination of computed space-filling models indicate that the distortions of the metal coordination



**Scheme 1** Synthesis of Schiff-base macrocyclic helicates. *Reagents and conditions*: i, $K_2CO_3$, DMF, reflux; ii, iron filings, AcOH, aq. EtOH, reflux; iii, [2 + 2] cyclocondensation, pyridine-2,6-dicarbaldehyde, $Ag(ClO_4)\cdot H_2O$, MeOH, reflux; iv, transmetallation, 5 $M(ClO_4)_2\cdot 6H_2O$, MeCN, room temp. ($M = Co^{II}, Ni^{II}, Zn^{II}$).

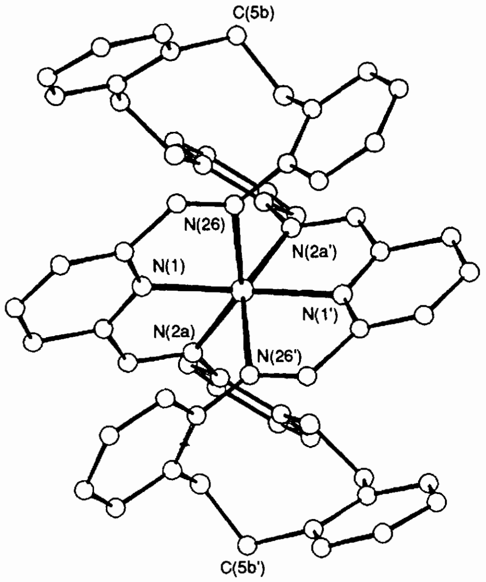


**Fig. 1** The molecular structure of $[M(\mathbf{1})]^{2+}$ ($M = Co^{II}, Ni^{II}, Zn^{II}$), illustrated by $[Zn(\mathbf{1})]^{2+}$ viewed parallel to the twofold rotation axis. The principal bond lengths (Å) and angles (°) are: $Co^{II}$ M–N(1) 2.035(8), M–N(2a) 2.143(7), M–N(2b) 2.272(8), N(1)–M–N(1′) 151.1(3), dihedral angle 80.0. $Ni^{II}$ M–N(1) 1.996(7), M–N(2a) 2.138(7), N–N(2b), 2.168(7), N(1)–M–N(1′) 158.5(3), dihedral angle 84.2. $Zn^{II}$ M–N(1) 2.023(12), M–N(2a) 2.139(12), M–N(2b) 2.373(13), N(1)–M–N(1′) 146.3(5), dihedral angle 75.7. The dihedral angle is the angle between planes N(1)N(2a)N(2b) and N(1′)N(2a′)N(2b′).

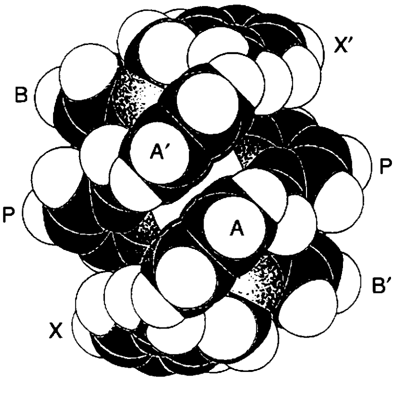


**Fig. 2** Computed space-filling diagram of the X-ray structure of $[Zn(\mathbf{2})]^{2+}$ viewed parallel to the molecular two-fold axis showing two symmetry-related three-tier π-stacks comprising xylenyl (X), pyridinediyl (P) and iminophenoxy (B) aromatic rings and the offset face-to-face orientation of the symmetry-related iminophenoxy (A) rings. Dihedral angles, A–A′ 8.7, B–P′ 17.6, X–P′ 17.1°; offsets, A–A′ 2.5, B–P′ 0.5, X–P′ 3.1 Å; interplanar distances, A–A′ 3.6, B–P′ 3.6, X–P′ 3.0 Å.

geometries originate in the different positions of the two crystallographically independent iminophenoxy rings, A and B, of the ligand (Fig. 2). While one iminophenoxy ring (B) lies in a face-to-face relationship with the pyridine ring, the other iminophenoxy ring (A) is orientated in a face-to-face position with its symmetry equivalent (A′). These, together with xylenyl–pyridyl interactions result in two symmetry-related three-tier stacks giving a total of five instances where pairs of aromatic rings lie in orientations associated[8] with favourable arene–arene interactions in the molecule. Aromatic π–π interactions between individual ligand strands stabilise the structures of many non-macrocyclic helicates,[1–4] and our observations identify a new role for aromatic interactions in stabilising structures of macrocyclic complexes; in these cases, compression of the ligand cavity is facilitated so that a single, relatively small metal ion may be accommodated in the large 34-membered ring.

Both $^1H$ and $^{13}C$ NMR spectra of $[Zn(\mathbf{1})]^{2+}$ in $[^2H_3]$acetonitrile show resonances corresponding to one quarter of the molecule indicating that the complex possesses $D_2$ symmetry on the NMR timescale. Crucially, the observation of diastereotopic environments for the methylene protons of $[Zn(\mathbf{1})]^{2+}$ at ambient temperature, evidenced by the AB multiplet at δ *ca.* 4.6 in its $^1H$ spectrum, is consistent with the retention of a helically chiral structure for the complex in solution. A number of dynamic processes that produce appropriate exchanges of ligand environments to give a $D_2$ 'time-averaged' structure can be envisaged, *e.g.* a helix bending-twisting process similar to that proposed by Lehn *et al.* for $Cu^I$ oligobipyridine helicates,[2] and variable temperature NMR investigations of these processes are underway.

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## Footnotes

† *Crystal data* for $[Co(\mathbf{1})](ClO_4)_2(MeCN)_2$: $C_{58}H_{48}N_8O_{12}Cl_2Co$, $M_r$ = 1178.90, orange crystal (0.40 × 0.29 × 0.26 mm$^3$); monoclinic, space group *C*2/*c*, with $a$ = 14.881(3), $b$ = 18.786(3), $c$ = 19.866(3) Å, β = 104.70(2)°, $U$ = 5371.80 Å$^3$, $D_c$ = 1.458 g cm$^{-3}$, $F(000)$ = 2436, μ(Mo-Kα) = 4.80 cm$^{-1}$. $R$ = 0.0706 for 1697 unique reflections having $I/\sigma(I) \geq 3.0$ and 207 variables. For $[Ni(\mathbf{1})](ClO_4)_2(MeCN)_2$: $C_{58}H_{48}N_8O_{12}Cl_2Ni$, $M_r$ = 1178.68, red crystal (0.38 × 0.20 × 0.18 mm$^3$); monoclinic, space group *C*2/*c*, with $a$ = 14.680(3), $b$ = 18.609(3), $c$ = 20.085(4) Å, β = 104.08(2)°, $U$ = 5321.98 Å$^3$, $D_c$ = 1.471 g cm$^{-3}$, $F(000)$ = 2440, μ(Mo-Kα) = 4.86 cm$^{-1}$. $R$ = 0.0684 for 1829 unique reflections having $I/\sigma(I) \geq 3.0$ and 208 variables. For $[Zn(\mathbf{1})](ClO_4)_2(MeCN)_2$: $C_{58}H_{48}N_8O_{12}Cl_2Zn$, $M_r$ = 1185.31, yellow crystal (0.30 × 0.13 × 0.11 mm$^3$); monoclinic, space group *C*2/*c*, with $a$ = 14.894(3), $b$ = 18.800(3), $c$ = 19.793(3) Å, β = 104.82(2)°, $U$ = 5346.99 Å$^3$, $D_c$ = 1.472 g cm$^{-3}$, $F(000)$ = 2448, μ(Mo-Kα) = 5.79 cm$^{-1}$. $R$ = 0.0759 for 1033 unique reflections having $I/\sigma(I) \geq 3.0$ and 149 variables.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ $[Ag_2(\mathbf{1})](ClO_4)_2\cdot\frac{1}{2}MeCN$: $^1H$ NMR (250.1 MHz, $CD_3CN$, 298 K): δ 8.46 (s, 2H), 7.81 and *ca.* 7.58 ($AB_2$ m, $^3J$ 7.7 Hz, 3H), 7.30 (ddd, $^3J$ 8.3, $^3J$ 7.2, $^4J$ 1.7 Hz, 2H), 7.17 (dd, $^3J$ 8.3, $^4J$ 1.3 Hz, 2H), *ca.* 6.94–6.89 (m, 6H), 6.84 (dd, $^3J$ 7.9, $^4J$ 1.7 Hz, 2H), 5.12 (s, 2H). MS [FAB$^+$ in *m*NBA (*meta*-nitrobenzyl alcohol) matrix]: *m/z* 1154 (29%, $M^+ - ClO_4$), 1055 (7, $M^+ - 2ClO_4$), 948 [100, $M^+ - (Ag + 2ClO_4)$], 527 [20, $M^{2+} - 2ClO_4$]. $[Co(\mathbf{1})](ClO_4)_2$: MS (FAB$^+$ in *m*NBA matrix): *m/z* 997 (100%, $M^+ - ClO_4$), 898 (77 $M^+ - 2ClO_4$). $[Ni(\mathbf{1})](ClO_4)_2$: MS (FAB$^+$ in *m*NBA matrix): *m/z* 995 (100%, $M^+ - ClO_4$), 896 (90, $M^+ - 2ClO_4$). $[Zn(\mathbf{1})](ClO_4)_2$: MS (FAB$^+$ in mNBA matrix): *m/z* 1002 (100%, $M^+ - ClO_4$), 903 (52, $M^+ - 2ClO_4$). $^1H$ NMR (250.1 MHz, $CD_3CN$, 298 K): δ 8.10 (t, $^3J$ 7.7 Hz, 1H), 7.80 (s, 2H), 7.66 (d, $^3J$ 7.7 Hz, 2H), 7.27 (ddd, $^3J$ 8.0, $^2J$ 1.6 Hz, 2H), 7.10 (m, 2H), 6.97 (dd, $^3J$ 8.2, $^4J$ 1.2 Hz, 2H), 6.86 (ddd, $^3J$ 7.6, $^4J$ 1.2 Hz, 2H), 6.36 (m, 2H), 6.29 (dd, $^3J$ 7.8, $^4J$ 1.6 Hz, 2H), 4.63, 4.65 (AB m, $^2J$ 11.4 Hz, 4H). All compounds gave satisfactory analyses for C, H and N.

§ $^1H$ and $^{13}C$ NMR spectra of the bimetallic precursor complex $[Ag_2(\mathbf{1})]^{2+}$ in $CD_3CN$ also show resonances corresponding to one quarter of the ligand in the complex. However, while the $^1H$ methylene subspectrum shows a singlet ($A_2$) pattern at 298 K, on lowering the temperature it becomes a broad doublet at 253 K before sharpening to resemble a broadened AB multiplet at 233 K. The chemical shift non-equivalence of methylene protons at low temperature is consistent with a chiral structure for $[Ag_2(\mathbf{1})]^{2+}$, perhaps involving helicity in the macrocyclic ligand, while loss of chirality at higher temperatures corresponds with rapid exchange of metal ions between ligand-coordinated and solvated environments, *e.g.* $[Ag(MeCN)_n]^+$, consistent with the lability shown by the disilver complex in transmetallation reactions.

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